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ELECTRODE MIGRATION AND REACTION PROCESSES

OCCURRING WITHIN.

ALKALINE-ZINC BATTERIES

Contract No. AF 33-615)-3292

Fourth Quarterly Technical Progress Report

for the period

1 September 1966 to 1 December 1966

NOTICE

DEPARTMENT OF CHEMISTRY

CALVIN COLLEGE

Grand Rapids, Michigan

Investigation of the Electrode Migration and Reaction Process Occurring in

Alkaline-Zinc Batteries

Contract No. AF 33(615)-3292

Quarterly Technical Progress Report

No. 4

Period: 1 September, 1966 to 1 December 1966
Prepared by: T. P. Dirkse

FOREWORD

This report was prepared by Calvin College, Grand
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stitute approval by the Air Force of the findings or conclusions contained
herein. It is published for the exchange and stimulation of ideas.

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ABSTRACT

A review of the literature dealing with zinc electrode processes is given. The
processes reviewed are: anodic behavior; cathodic behavior; and corrosion be-
havior. Suggestions are also made as to areas where experimental information is,
as yet, not incorporated in the published literature.

The solubility values of various types of zinc oxide in KOH solutions at about 0°C
is presented.

LITERATURE REVIEW FOR THE ZINC ELECTRODE IN ALKALINE SOLUTIONS

Introduction

Metallic zinc is a widely used anode in batteries. There are several reasons for this. It has a high electrode potential in aqueous solutions, it is in good supply, and it can be used over a wide pH range. In many of the older battery systems zinc was often used in acid solutions, e.g., the Daniell cell, the Grove's cell, and the dichromate cell. A good historical review of these and similar cells is given by Vinal (77). Zinc also was one of the metals used by Volta in his pioneering work on batteries (78).

Today, however, batteries which use zinc as the negative electrode (or anode) are either the Leclanche cell or one of a variety of alkaline systems. These alkaline systems often employ a KOH solution as the electrolyte. They differ in the cathode (or positive plate) that is used. There is, e.g., the Ruben cell which uses mercuric oxide as the cathode, the Lalande cell which uses cupric oxide, the air depolarized cell, and the silver-zinc cell. From time to time interest has also been shown in a nickel-zinc system. Thus, there is a variety of systems which employ the zinc anode with an alkaline electrolyte. Some of these are primary cells, some secondary, and some are both.

Because of the widespread interest in zinc-alkaline systems it is fitting that a review be made of the work that has been done on the electrochemical behavior of zinc in alkaline solutions. Generally speaking, the zinc electrode represents the weak link in zinc-alkaline battery systems and unless improvements can be made in the behavior and performance of the zinc electrode, no great progress will be made in the development of zinc-alkaline battery systems.

This can be illustrated by the silver-zinc battery system. This system has a potentially high energy density value. Yet this has not been realized for a secondary silver-zinc battery. This is mainly due to the performance of the zinc electrode. This electrode, when working in alkaline solutions, has two main weaknesses:

    1- it will not accept charge efficiently at low temperatures, e.g., $5^\circ C$;

    2- it loses capacity as it cycles.

If, in some way, these weaknesses could be overcome, then the performance of the silver-zinc battery would be better with respect to cycle life, operating temperature range, and current density. Improvements here would lead to a larger energy density value for this system. These same improvements might well be used to advantage in other secondary zinc-alkaline systems, e.g., the zinc-oxygen system.

A considerable amount of work has been done on the zinc electrode, particularly during the past ten years. The present review is an attempt to correlate this work, with the hope that out of this review will arise suggestions and guidelines for further work in this area. Hopefully, also, this review may suggest that there is some legitimate optimism that improvements can be made.

For purposes of organization the following outline will be followed:

        A--Anodic behavior, i.e., discharge reaction.

        B--Corrosion behavior, i.e., open circuit stand.

        C--Cathodic behavior, i.e., charge reaction.

        D--Miscellaneous

As a help in getting a quick over view of the zinc electrode, a potential-pH diagram is given on Figure 1. This is a simplified diagram. More complete diagrams are given elsewhere (9, 5). The diagram on Figure 1 has values for the main species to be discussed in this review. The placement of some of the lines, e.g., for $Zn(OH)_2$, will be altered by using different crystal modifications of $Zn(OH)_2$. However, these are minor points for the present discussion and Figure 1 is intended to show merely the general areas where the various species are stable. Lines for oxygen and hydrogen formation are also given. For battery work, the area of interest is at the extreme right of the figure, at pH values above 14. It is to this general area that we shall make occasional reference.

A--<u>Anodic Behavior</u>.

Most of the published work on the zinc electrode processes in alkaline solutions has dealt with the anodic process. This process has been studied in a variety of ways. Some studies used galvanostatic methods (23, 35, 36, 41, 50, 69); others used transient DC pulses (48, 49, 55); and the potentiostatic approach has also been used (68). The process has been studied in dilute as well as in concentrated alkaline solutions. Both NaOH and KOH have been used as the electrolyte. Thus a good deal of experimental information is available. A typical current-voltage curve is shown on Figure 2. The dotted line here represents the onset of passivation.

While there are some minor differences in detail and emphasis, the general conclusion of all this work is that the anodic process consists of the following steps.

    1--the zinc is oxidized to form solid ZnO or $Zn(OH)_2$;

2—this ZnO or $Zn(OH)_2$ dissolves in the electrolyte to form $Zn(OH)_3^-$ or $Zn(OH)_4^=$, depending on the electrolyte concentration;

3—after a while the electrolyte can no longer dissolve the ZnO or $Zn(OH)_2$ that is produced by the charge transfer reaction, and then the solid ZnO or $Zn(OH)_2$ film forms on the electrode, passivating it.

Step 3 would represent the end of discharge in a zinc-alkaline battery.

Qualitatively, this interpretation is supported by the following observations;

a—The current density at which passivation occurs decreases with decreasing KOH concentration (38). At these lower KOH concentrations, zincate is less soluble and consequently the passivating layer precipitates out of solution sooner.

b—The current density at which pasivation occurs decreases with increasing zincate content of the electrolyte (38). Such solutions cannot dissolve as much of the ZnO or $Zn(OH)_2$ formed during the charge transfer process.

c—The current density at which passivation occurs decreases with a decrease in the rate of stirring (38).

d—The pasivation time for the zinc electrode increases with decreasing current density (25).

e—A report on some work that was done to improve the low-temperature discharge performance of the zinc electrode (42). Since zinc is an active metal it is very likely that a thin film of oxide is present on any zinc metal in contact with an aqueous solution, Fig. 1. When special care was taken to remove this oxide film, the discharge performance was considerably improved at -65°F. However, when the electrode was allowed to stand in the electrolyte for 12 hours before discharge, the performance was poor. This was attributed to the formation of a film formed by corrosion during the 12 hour stand.

f—The discharge capacity of the zinc electrode is proportional to the amount of KOH present per unit area of zinc (70), Fig. 3. The extra KOH will dissolve more ZnO or $Zn(OH)_2$ before the pasivating film is formed.

g—The discharge capacity of the zinc electrode shows an increase with increasing KOH concentration up to about 10 M and then it shows a sharp decrease (70). This decrease will be discussed later.

h—The discharge capacity of the zinc electrode increases with increasing surface area (71).

While there is general agreement on the three-step mechanism for the anodic behavior, there is some difference of opinion concerning the deta 's of the various steps. Part of this may be due to differences in experimental procedure and conditions. Euler (22) suggests that the parameters for the electrode process may depend on the length of time the electrode stands in the alkaline solution. They also depend on the purity of the zinc electrode.

Step 1

The charge transfer process (step 1) may proceed in one of two ways. Several (55, 68, 69, 81) have suggested that the charge transfer results in the formation of zinc ions. This takes place

$$Zn \rightarrow Zn^{++} + 2e \qquad (1)$$

in alkaline solutions at a potential of about -1.1 to -1.2 volts. These zinc ions are immediately coordinated by the hydroxide ions to give a zincate ion.

$$Zn^{++} + 4OH^- \rightarrow Zn(OH)_4^= \qquad (2)$$
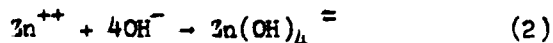
Another mechanism for the charge transfer step has been suggested recently (8).

$$Zn + OH^- \rightarrow Zn\ OH + e \qquad (3)$$

$$ZnOH + OH^- \rightarrow Zn(OH)_2 + e \qquad (4)$$
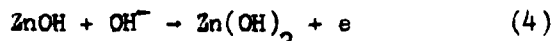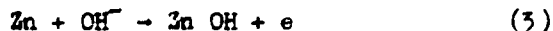
Reaction (4) is considered the rate-determining step.

It is difficult to make a choice between these two mechanisms. The first one really assumes no formation of ZnO or $Zn(OH)_2$. However, reaction (2) could also be considered to proceed in two steps

$$Zn^{++} + 2\ OH^- \rightarrow Zn(OH)_2 \qquad (5)$$

and

$$Zn(OH)_2 + 2\ OH^- \rightarrow Zn(OH)_4^= \qquad (6)$$
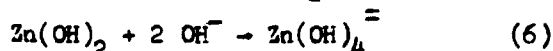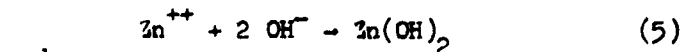
Thus either of these mechanisms could be used to account for the formation of the $Zn(OH)_2$. Experimentally, no key experiment has been devised yet that unequivocally selects one of these mechanisms. Many of the experimental techniques and approaches that are used at inert electrodes cannot be used here. The electrode itself is electrochemically active, and the nature and area of the surface change during anodization. At this point there is little to be gained by selecting one mechanism or the other.

Step 2

The formation of Zn^{++} or ZnO or $Zn(OH)_2$ is a function of the current density. The rate of formation of this discharge product can be calculated and controlled. This is followed by Step 2, the dissolution of the discharge product in the electrolyte to form zincate ions. It is here that there is a great dearth of information. This is due to the fact that the nature of the discharge product is unknown. It could be ZnO, $Zn(OH)_2$, or $Zn(OH)_2(H_2O)_2$. Furthermore, various types of $Zn(OH)_2$ have been described. It may, and likely is, some species that is unknown and has but a transient existence.

To understand the anodic zinc process it is necessary to know the rate at which this discharge product dissolves. Landsberg (51, 52) has carried out some work on the rate of dissolution of ZnO in KOH or NaOH solutions. It is questionable, however, whether this information will have much bearing on the problem. This is due to the fact that the discharge product, whether it be ZnO or $Zn(OH)_2$, seems to be quite different from any similar product that is known.

The film that is present on a pasivated electrode is, after treatment to prepare it for experimental investigation, ZnO. So is the white material some times formed as a precipitate during low rate discharges of zinc-alkaline cells. The solubility of such ZnO in KOH solutions has been measured. But the discharge product at the zinc electrode is much more soluble than this. In fact, solutions of KOH were saturated with ZnO and then used as the electrolyte for the anodic treatment of a zinc electrode (14). Anodization was continued until a precipitate appeared in the electrolyte. At that time the zincate content of the solution was about twice that at the beginning of anodization. It appears that, in general, the solubility of the discharge reaction product is about twice that of any available ZnO.

A separate phase of this contract deals with the solubility of ZnO in KOH solutions, so this problem will be discussed more fully in another report. However, no kind of ZnO yet available has a solubility anywhere near that of the discharge reaction product. This latter ZnO or $Zn(OH)_2$ must be a transient, highly soluble species. Because it is an unknown type and very likely a transient or unstable species, it is not available for experimentation. It does undergo changes with time. A KOH solution saturated with this material gradually precipitates out stable ZnO and the zincate content of the solution slowly approaches that of a solution saturated with stable ZnO. This process is very slow. We have noted changes over a period of 9 months at room temperature.

Moreover, it is likely also that this same discharge product, if present on the electrode surface, will also undergo a recrystallization or a phase change to a stable ZnO or $Zn(OH)_2$ (25). It is this form which apparently is observed when

passivating films are prepared for observation.

At the moment, then, the nature and solubility of this anodic product remain unknown. Some attempts were made to determine the solubility of anodically produced $Zn(OH)_2$ in KOH solutions. The results, however, were rather irreproducible (13). This is to be expected because of the time-dependence of the solubility. Undoubtedly, kinetic effects are involved here. It could be enlightening to take the X-ray diffraction pattern of the electrode while it is being anodized. The method developed by Burbank and Wales (7) seems the best available for this.

Step 3

Step 3 is the passivating reaction. Many attempts have been made to determine the time-dependence of this process. One relationship that has been observed (3, 21, 31, 48, 49, 50) is given in equation (7)

$$(i-a) \ t^{1/2} = k \qquad (7)$$

where
    i is the current density;
    t is the time to reach passivation;
    a is a constant, probably a limiting current density; and
    k is a constant

This relationship was observed for both vertical and horizontal electrodes (31, 32).

This equation is similar to one for a diffusion-limited process. In this situation it could be the diffusion of zinc ions away from the electrode. If one uses the Sand equation (67) then

$$k = \frac{nFAD^{1/2} \ \pi^{1/2}C}{2} \qquad (8)$$

where
    n is the valence of the diffusing ion;
    F is the Faraday;
    D is the diffusion coefficient of the diffusing ion;
    C is the difference in concentration of the diffusing species at the electrode surface and in the bulk of the solution.

Application of equation (8) may not be easy in this situation. The diffusion current of the zincate ion does vary with KOH concentration (12c) and there may be changes in OH^- ion concentration due to reactions 2-6. Furthermore, convective processes will no doubt modify the diffusion process. However, if one assumes that the diffusion coefficient does remain constant then the fact that k is experimentally a constant, suggests that C remains constant throughout the anodic process.

Assuming an average value of 0.7 amp. $\sec^{1/2}/cm^2$ for k (32) and using 10^{-6} cm^2/sec as the value of the diffusion coefficient (12c, 60c), then at $25^\circ C$. the value of O is approximately 0.004 moles/cc or 4 M. This is a solubility greater than that of stable ZnO but possibly that of the discharge reaction product. This value seems fairly reasonable considering the obvious approximations involved in making the calculations.

Equation (8) could account for the decrease in the value of k above about 8.5M KOH. Dalin and Stackurski (12c) found the diffusion coefficient of zincate ion to decrease sharply in KOH concentrations above 7 M. However, below 7 M KOH the diffusion coefficient was fairly constant.

At higher current densities, a first order time dependence was found (3, 50)

$$(i-a') \ t = k' \tag{9}$$

a' has been interpreted as a corrosion current density and k' as the number of coulombs needed to form a covering layer on the zinc electrode (3). Others (69) could determine no relationship between current density and passivation time.

The general interpretation for these relationships is that a or a' corresponds to the rate at which the discharge product dissolves in the electrolyte. i, of course, is a measure of the rate at which the zinc is oxidized. Thus equations (7) and (3) provide a mathematical statement of the proposition that the time required for passivation depends on the net effect of two processes: the formation of the discharge reaction product; and the dissolution of this product in the electrolyte. The greater the difference between these two processes, the faster the discharge reaction product will accumulate on the electrode surface and the shorter will be the time required for the electrode to be passivated. The term a can then be considered to be the maximum current density at which passivation will not occur (21). However, these relationships have not yet served to clarify in detail the mechanism of these anode processes.

The values of a, a', k, and k' have been determined over a range of KOH concentrations and a representative set of values is given on Figure 4. These values whatever their significance, both pass through a maximum between 8 and 11 M KOH (3, 32, 41).

Earlier in this report reference was made to the work of Shepherd (70) in which he found that the discharge capacity of the zinc electrode passed through a maximum at about 10 M KOH.

There are other phenomena also that are similarly related to the KOH concentration. Above 10 M KOH there is a sharp increase in the hydrogen overvoltage at the zinc electrode (37). Below 10 M KOH the hydrogen overvoltage decreases with increasing KOH concentration.

It has been found that the rate of dissolution of ZnO increases with increasing KOH concentration up to 10 M KOH and then it decreases as the KOH concentration increases from 10 to 16 M (51). As noted earlier, the diffusion coefficient of zincate ion was found to increase markedly when the KOH concentration increased beyond 30% (12c).

While this matter of maxima or minima in certain values at about 30 to 40% KOH seems to be generally recognized, relatively few attempts have been made to account for this. It would appear that these phenomena would be related to the physical characteristics of KOH solutions. Yet there are no discontinuities in the physical values. This can be seen on Figures 5-9, where the density, viscosity, specific conductance, surface tension, and activity of KOH solutions are shown. Only with specific conductance is there an inversion point and this occurs at about 7 M or 30% KOH.

One suggested interpretation is that the solubility of the anodic discharge product passes through a maximum at 8.5 M KOH (31). As noted earlier (51) the rate of dissolution of ZnO changes at about 10 M KOH. This may be fully as significant as the amount dissolved at equilibrium because the net effect of the rates of formation and the rate of dissolution of the anodic product determines when an electrode becomes passivated. But it should be noted that this work on the rate of dissolution of the ZnO was carried out with a stable form of ZnO and not with the discharge reaction product.

Another explanation is that the maxima on Fig. 4 may be the result of the combined effects of the increase of convection due to the ability of KOH to dissolve more of the anode product as the concentration of KOH increases, and the increase of viscosity at the same time which decreases the convective effect (32). This work was done with vertical electrodes in excess KOH solution and undoubtedly such convective effects modified the results. However, since these maxima are also observed under other conditions when convective effects are not as prominent, this does not seem to be as good an explanation as the first one given.

Shepherd (70) suggests that these maxima are also related to the solubility of the anode product. He suggests that at 10 M KOH the solubility of ZnO in KOH shows a decrease. This, however, is based on equilibrium data, i.e., the % KOH is expressed as free OH^- ion exclusive of the hydroxide ions used to form the zincate (16). Work currently in progress shows that the solubility of ZnO increases with increasing KOH concentration up to at least 12 M (about 45%). We have not used higher concentrations of KOH.

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It appears that at present the most likely explanation is one which assumes that the rate of dissolution of the anodic product decreases with KOH concentration above 10 M. Undoubtedly other factors, such as convection, modify this behavior in any given case. This assumption will account for the changes in the rate of passivation of the zinc electrode but it does not appear to offer an explanation for the other phenomena that also have maxima at about 8.5 to 10 M KOH. Nor is there yet an explanation why the rate of dissolution of ZnO should decrease in KOH concentrations about 10M.

Assuming the above general mechanism for this anodic zinc process, then it would appear that the passivation time, the discharge capacity, or limiting current density would be affected by other factors such as zincate concentration in the electrolyte, the temperature, the cation in the electrolyte, the time, and the presence of impurities or foreign materials. None of these has really been explored thoroughly, but the following is a summary of what has been done.

Effect of Zincate Concentration

Some general observations about the influence of the zincate ion have been made. Passivation times were found to be less reproducible when zincate ions were present (3) but no explanation was attempted. The limiting current density was found to decrease in the presence of zincate ions (38) and the reaction of zinc with the KOH solution was also found to decrease in the presence of zincate ions (4). Qualitatively, these results can readily be explained. The presence of zincate decreases the amount of additional zincate that can be dissolved and likely then also the rate at which the anodic product dissolves in the electrolyte.

During galvanostatic measurements it was found that the voltage-time curves were altered significantly by the presence of zincate ions (69). Similarly, the voltage-current curves obtained during potentiostatic experiments were displaced in the presence of zincate ions (68). This was found in 0.01 and 0.1M KOH solutions where the amount of zincate in solution is almost vanishingly small. It was suggested that these curves were affected by the adsorption of anions on the electrode surface and that possibly the zincate ions are preferentially absorbed. This seems a likely possibility but there is very little information available that can be used to test this hypothesis.

As the anodic current density is gradually increased it was found that the electrode often became passivated at a lower current density when zincate ion was present, Figure 10. This was true in a range of KOH concentrations of 20-45% at room temperature. It was not so common when the electrode was amalgamated. These results are to be expected if one accepts the general outline for the anodic zinc process. Solutions already containing zincate cannot dissolve as much additional zincate as those containing no zincate. Consequently the pasivating film forms or precipitates earlier.

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In addition, the presence of zincate also appeared to lower the overvoltage at which the anodic reaction proceeds, Figure 11. This, too, was found to be the case in all KOH concentrations used, but the difference was less in 45% KOH. There is no ready explanation for this. Even when KOH solution containing no zincate is used as the electrolyte, zincate is soon produced as a result of the anode reaction. It is, of course, present in smaller amounts so there is the possibility that this is a function of the zincate concentration.

Effect of Temperature

Very little work has been reported on the effect of temperature on the anodic zinc process. The limiting current density decreases with decreasing temperature (14, 38) and Shepherd (70) observed a change in the capacity of the zinc electrode per unit weight of KOH, Figure 12.

The variation of the limiting current density with temperature has been attributed to the increase in solubility of zincate with increasing temperature. However, the effect of temperature on the solubility of ZnO in KOH solutions is very slight, Figure 13, and, until shown otherwise, one would assume that the solubility of the anodically produced zincate follows the same pattern. This means that the temperature variation of the limiting current density can not be attributed to the solubility of zincate. One possible explanation is that the viscosity the electrolyte increases with decreasing temperature, allowing the zincate to diffuse away from the electrode less rapidly. As a result the zincate concentration at the electrode surface builds up more rapidly at lower temperatures.

The anodic zinc process has been studied by means of a voltage sweep technique (18). There, too, it was found that the electrode passivates earlier the lower the temperature. The temperature range used was 0° to 50°C. When the process was studied as a function of KOH concentration at each temperature, it was found that the passivation time or current density passed through a maximum and the maximum appeared at lower KOH concentrations the lower the temperature. Here again the maximum may be the net effect of at least two processes. One is the increasing solubility of ZnO with increasing KOH concentrations. The other is the increased viscosity of increasing KOH concentrations allowing for slower diffusion of zincate away from the electrode surface (14). Since the solubility of ZnO in KOH is almost temperature independent, the effect of temperature then would be entirely due to the viscosity change. Consequently, the maximum would be found at lower KOH concentrations at lower temperatures.

Effect of Cation

Most alkaline battery systems using zinc anodes have a potassium hydroxide solution as the electrolyte. Occasionally a sodium hydroxide solution is used (56). There are differences in viscosity, freezing points, and ZnO solubility. Although it appears that the OH^- ion rather than the cation is involved in the zinc electrode processes, yet some of these processes involve ionic diffusion and this is influenced by the viscosity of the electrolyte. Consequently, differences between NaOH and KOH may not be directly due to the difference in cation but to differences, e.g., in viscosity. This, of course, may be related to the difference in extent of hydration of the cation.

It has been observed that equations (7) and (9) apply to different ranges of current density or electrolyte concentration when NaOH is substituted for KOH (3). This has been attributed to differences in viscosity, that of NaOH solutions being higher.

Some work has also been done using RbOH and CsOH solutions as the electrolyte (73). In general, KOH is the best alkali hydroxide for use with the zinc electrode.

Effect of Time

In determining the limiting current density at which the zinc electrode can be anodically oxidized without becoming passive, it has often been noted that the limiting current density so obtained depends largely on the length of time the electrode is allowed to operate at a given current density. The shorter the time interval at each current density, the higher the limiting current density will be. Time is also very important in making potentiostatic measurements (68). Depending on the time the electrode is allowed to stand at a given potential, it may or may not reach equilibrium. All of this points up the fact that kinetic effects are important factors in the anodic zinc process. Not all the processes proceed rapidly.

Electrode Composition

The physical nature of the zinc electrode also has an effect on these anodic processes. Shepherd (72) found that the zinc grain structure influenced the discharge capacity. Annealed zinc gave the best discharge capacity while quenched zinc had the poorest. Rolled zinc had an intermediate discharge capacity.

Ordinarily the zinc used in alkaline batteries is alloyed with small amounts--up to 2%--of mercury. Shepherd (72) studied the effects of many metals when alloyed with zinc. He used amounts up to 5% and concluded that mercury was the only metal that definitely improved the performance of the zinc electrode under all conditions.

The effect of mercury is to raise the hydrogen overvoltage and thus minimize
the self discharge reaction of the zinc electrode. However, amalgamation also has
an effect on the anodic processes (18). Amalgamated zinc electrodes have a lower
anodic overvoltage over a temperature range of 0° to $50^\circ C$ and have a higher limit-
ing current density, i.e., they do not passivate as readily as unamalgamated
electrodes, Figures 10 and 11. This effect is observed in 20 to 45% KOH although
the difference is not large in the higher KOH concentrations. The effect of sil-
ver contamination on these processes is very slight (18).

No explanation has yet been given for the beneficial effect of amalgamation on the
anodic processes. This may be due to the fact that little attention has been paid
to this aspect of the problem. Apparently the amalgamation interferes with the
formation of the passivating film. This is an area in need of further investiga-
tion.

Nature of the Passivating Film

Attempts have been made to determine the nature of the passivating film. Experimen-
tally, it is readily observed that films form on the zinc electrode and these films
may have different colors. The question that has not been resolved yet is whether
the passivating film is formed by (1) the precipitation of ZnO from a supersaturated
zincate solution; or (2) the formation of ZnO directly on the surface of the metal.
As zincate ions are formed, equations (2)-(6), the OH^- ion concentration does de-
crease locally. This decreases the ability of the surface film to dissolve more
zincate. At present it is not possible to determine which mechanism is the correct
one.

Some suggestions as to the nature of the passivating film are: rhombic $Zn(OH)_2$
(38), an "aged" form of $Zn(OH)_2$ (25), an adsorbed layer of O and OH (62), and
ZnO (36, 45). The film present at the moment the electrode is passivated has a
metallic appearance (14, 35, 41). A dark colored film is often observed on a
zinc electrode. It is generally agreed that this is not the passive film (14, 35),
but is a zinc oxide that has excess interstitial zinc atoms (48, 53, 68). While
there is agreement on this, there is not agreement as to the nature of the passive
film. This, too, has still to be determined and perhaps the technique developed
by Burbank and Wales (7) could provide at least the beginning of an answer. Some
attempts have been made to examine the film by electron diffraction (81) and the
conclusion was that the film is not definitely crystalline. The crystalline struc-
ture appears after prolonged polarization. It is still necessary, however, to de-
vise some way of examining the film as it is formed because it undoubtedly does
undergo changes with time.

In conclusion, there are many facets of the anodic zinc processes that are unknown.
Obviously, we are dealing here with several simultaneous processes that are time-
dependent. The processes themselves have not been clearly identified and certainly

the rates and the rate determining factors are unknown. In general, these processes are:

    a- dissolution of the product formed by the charge transfer process;

    b- diffusion of the solute species, e.g., OH^-, and zincate;

    c- decomposition of zincate to form ZnO;

    d- phase changes of the precipitated ZnO.

Some problems that should be dealt with in this connection are:

    a- study the film formation using the Burbank and Wales approach (7);

    b- attempt to determine the solubility maximum and the rate of decomposition of electrolytically produced zincate;

    c- study the adsorption at the zinc electrode.

When the anodic process is continued beyond passivation of the zinc electrode, oxygen is formed and evolved. Little study has been made of this process and generally it is of little significance in a zinc-alkaline battery unless a cell in a battery is discharged completely and may reverse polarity. Jirsa and Loris (39) contended that this oxygen was produced by the decomposition of oxides in which zinc has an oxidation number greater than +2. However, this has not been substantiated by others.

B- Corrosion Behavior

It can be seen from Figure 1 that metallic zinc is oxidized in KOH solutions with the accompanying evolution of hydrogen. However, the evolution of hydrogen and the oxidation of zinc are affected by the high hydrogen overvoltage on zinc. Consequently, the reaction is not vigorous under ordinary conditions. Nonetheless, some reaction does occur. This amounts to a self-discharge of the zinc. The reaction can also accompany the charging reaction at the zinc electrode. This presents a problem for sealed cell operation. No simple way has been found yet to remove the hydrogen rapidly within a sealed cell.

Because this reaction presents a problem, especially for sealed cells, it has received some study. The problem here is one of controlling the hydrogen overvoltage. The presence of impurities often lowers the overvoltage but the presence of mercury increases it (82). Zinc electrodes in alkaline cells are generally amalgamated. However, they often contain other materials to act as binders, and

these substances may also affect the hydrogen overvoltage. This makes the problem complex. Data obtained on zinc metal may not quite apply to the situation existing in a battery. Some of these factors cannot be controlled. For example, it has been observed that a black film formed on a passivating zinc electrode acts as a catalyst for hydrogen evolution, i.e., it has a lower hydrogen overvoltage (60a). It has been estimated that the overvoltage is lowered at least 500 mv. Furthermore, zinc which partially penetrates a separator in a cell is not amalgamated, though the original zinc electrode was, and hence this zinc dendrite can serve as a site for the evolution of hydrogen (76).

So far as zinc electrodes are concerned, the hydrogen evolution is visible already at overpotentials of 30-50 mv. Thus, hydrogen evolution on zinc must take place at practially all potentials used during the charging process (12a). However, the exchange current density for the hydrogen reduction on zinc in 44% KOH without zincate was found to be 10^{-9} amp/cm^2. Because of this low value the evolution of hydrogen becomes significant only at overvoltages in excess of 100 mv.

The hydrogen overvoltage on zinc is also affected by the alkali concentration. There is a minimum at about 10 M for both NaOH and KOH but the values in NaOH are higher than they are in KOH solutions (2, 37). This was attributed to the difference in cation hydration and its effect on the double layer.

Furthermore, as corrosion proceeds the surface of the zinc may change due to physical changes taking place in the ZnO or $Zn(OH)_2$ that is produced (65). These changes may also result in a different value for the hydrogen overvoltage.

Snyder and Lander (74) studied the hydrogen evolution from commercial zinc electrodes containing 2% PVA and encased in a cellulosic separator material. They found that the amount of hydrogen evolved in a given time decreased as the electrolyte changed from 30 to 40 to 45% KOH. It decreased with increasing HgO content up to 4%, and it also decreased with decreasing temperature. Furthermore, the presence of zincate in the electrolyte increased the amount of hydrogen evolved. As a practical matter, it was also found that the rate of hydrogen evolution is too great for operation in a sealed cell when the zinc electrodes contained 1% by weight of HgO. With 4% by weight of HgO the electrodes had poor cycle life. Apparently the zinc electrode material had become too dense with a consequent decrease of surface area. Thus a 2% HgO content appears to be an optimum for sealed cell operation. However, this need not be true for all zinc electrodes. It may depend on what other materials are present, e.g., such as PVA

A further study of this reaction indicated that the rate of hydrogen evolution was some function of the activity of the water. It was suggested (74) that the following reaction is rate controlling

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad (10)$$
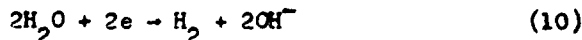
If this is true then the presence of zincate in the solution would increase the rate of hydrogen evolution because it reduced the OH^- ion concentration (by the formation of $Zn(OH)_4^=$) and thus raised the activity of the water.

Some work has been done on this corrosion reaction by measuring the weight loss of the zinc (8). This weight loss was then apparently converted to an equivalent current density and a plot was made of $\log i$ vs $\log a_{OH^-}$. A linear relationship was obtained with a slope of 0.4. If now one assumes that the H_2O rather than the OH^- ion is the source of the hydrogen one can replot the data as $\log i$ vs. $\log a_{H_2O}$. This gives a line with a slope of 1.6. This value corresponds to the coefficient for H_2O in the following equation

$$Zn + n\ H_2O \rightarrow H_2 + ZnO(H_2O)_{n-1} \qquad (11)$$
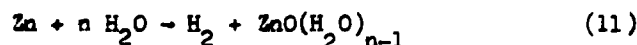
This could be interpreted to mean that the following reactions take place to about an equal extent.

$$Zn + H_2O \rightarrow H_2 + ZnO \qquad (12)$$

$$Zn + 2H_2O \rightarrow H_2 + Zn(OH)_2 \qquad (13)$$
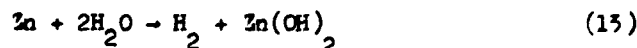
At this point, however, this suggestion is mere speculation.

The matter of hydrogen evolution at the zinc-electrode in a zinc-alkaline battery is still not clearly worked out. This is an almost insuperable problem because of the complexity of the situation. The rate of hydrogen evolution is a function of KOH concentration which changes, at least locally, during the cycling of cell. It changes with zincate concentration which also changes during a cycling. It is affected by the presence of impurities or additives. These may be incorporated in the zinc electrode, but they may also arise from other sources, such as degradation products of the separator or the presence of dissolved silver oxides (19). Furthermore, the net effect of a combination of factors is not necessarily additive.

It is somewhat surprising, however, that so little work has been reported on the parameters of hydrogen evolution on the zinc electrode in alkaline solutions. Hydrogen evolution is always a problem when zinc electrodes are used in alkaline solutions and efforts must be made to keep the hydrogen overvoltage as high as possible at the zinc electrode. However, it will be difficult to maintain this through the variety of changes that can occur in a zinc-alkaline cell in just one cycle. The nature of the cathode will, of course, affect this to some extent. This will determine what separators, if any, are needed, and it will determine which impurities are introduced into the solution. Thus, for a zinc-air cell, the changes during cycle would be less complex than for a silver-zinc cell. In the former cell, the hydrogen overvoltage throughout cycling might be fairly well predicted.

Some work has been done on the effect of impurities in or on the zinc electrode, i.e., impurities other than mercury. The way these impurities are incorporated in the zinc electrode influences the value of the hydrogen overvoltage. Small amounts of iron incorporated in the zinc electrode decrease the hydrogen overvoltage. But when these small amounts of iron were deposited on zinc in 10 M KOH, the hydrogen overvoltage was decreased to a greater extent (63). It was suggested that this was due to the formation of intermetallic compounds such as $FeZn_7$ or $FeZn_{13}$.

The presence of silver also increases the corrosion rate of zinc (19). When the silver is deposited from the electrolyte a solid solution of silver in zinc appears to form. This, too, then, lowers the hydrogen overvoltage, especially for amalgamated electrodes.(18).
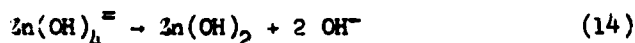
In conclusion, practically nothing is reported in the literature on the parameters of the zinc corrosion reaction in strongly alkaline solutions. Therefore work should be undertaken to measure these values as a function of amalgamation, KOH concentration, zincate concentration, and temperature. These values are needed so that we may know something about how this reaction proceeds in a fairly simple system. Admittedly, other factors that prevail in a working battery will modify these values, but at least, basic information will then be available against which one can determine the effect of certain cell peculiarities.
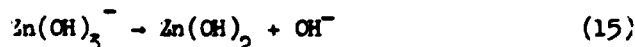

C-- Cathodic Behavior

The charging process at the zinc electrode is a cathodic one, i.e., a reduction is brought about. This reaction has, until recent years been the subject of very little investigation. This is the kind of reaction that takes place in an alkaline zinc plating bath. Such work has been done for many years but most of the reported work deals with a search for additives to improve the zinc plate. Little attention has been given to the mechanism of the reduction. Some work has been done on this reaction at the dropping mercury electrode, but there is always the question whether the mechanism is the same at a zinc electrode as at a dropping mercury or amalgam electrode.

In 1953 Gerischer (28) published a paper in which he discussed the theoretical relationship between the exchange current density and the concentration for the reduction of complex ions. Later (29) he applied this theory to the reduction of the zincate ion, $Zn(OH)_4^=$, at a hanging drop of zinc amalgam. He measured the variation of impedance with the frequency and concluded that for this reduction the transfer coefficient is 0.5 and the discharging species is $Zn(OH)_2$. This work was done at 25°C but little information is given about the composition or preparation of the solutions. Others (54) have also concluded that $Zn(OH)_2$ is the species involved in the charge transfer process.

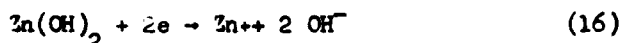Assuming that this conclusion is correct, then the discharge or cathodic reactic..
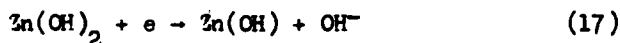mechanism is as follows

$$Zn(OH)_4^= \rightarrow Zn(OH)_2 + 2\ OH^- \tag{14}$$

or

$$Zn(OH)_3^- \rightarrow Zn(OH)_2 + OH^- \tag{15}$$

followed by

$$Zn(OH)_2 + 2e \rightarrow Zn^{++} 2\ OH^- \tag{16}$$

It is possible that reaction (3) is actually a two-step process, e.g.,

$$Zn(OH)_2 + e \rightarrow Zn(OH) + OH^- \tag{17}$$

$$Zn(OH) + e \rightarrow Zn + OH^- \tag{18}$$

Some polarographic work at a dropping mercury electrode did indicate a one-electron
step for this reduction (15). However, these solutions contained gelatin and later
work showed that gelatin does have a bearing on the kinetics of the reaction (17,
54). Consequently, the one-step reduction has not been proven experimentally, nor
has the mechanism of the zincate reduction at a metallic zinc electrode been
established. The reason for this, undoubtedly, is the experimental difficulty
of getting this type of information at the zinc electrode. As the reduction pro-
ceeds, zinc plates on to the electrode and this alters the surface area. Conse-
quently, the current density is not known nor can it be controlled. Furthermore,
since zinc is a fairly active metal there is always the possibility of local
corrosion and the presence of surface oxide films.

In an alkaline cell with zinc electrodes, the practical problem has been one of
the transport of zinc throughout the cell during cycling, and the formation of
zinc deposits which can grow into and through the separators. These factors
severely limit the cycle life of alkaline cells using zinc electrodes. Conse-
quently, in the past few years several programs have been undertaken to study the
nature of zinc growth and the conditions that control this. This work has been
reported in several places (12, 60, 61). In general, the conclusion in all this
work is that at low current densities a spongy or mossy deposit of zinc is ob-
tained while at higher current densities a more dendritic type of zinc deposit
is produced. These conclusions are based upon carefully controlled experiments.
Different authors, however, present somewhat different interpretations as to the
mechanism of the zinc deposit formation.

One such interpretation is that the predominant parameter is the over potential at
the zinc electrode during charging (60a). At low overpotentials, which also means

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lower current densities, the reaction is activation controlled and this gives rise
to mossy zinc deposits. At higher overpotentials (about 100 mv.) the reaction
is diffusion controlled and this produces a dendritic-type deposit. As protru-
sions penetrate the diffusion layer, spherical diffusion at the tips results in
preferential deposition and increased growth. No good explanation was found,
for the initiation of a surface dendritic formation although it was suggested that
this could be related to defects in the zinc electrode lattice. As current is
passed, the diffusion layer may thicken, but there is a point at which the pro-
trusions from the electrode surface are preferentially plated because they are
closer to the diffusion layer boundary than are depressions on the electrode sur-
face. If the diffusion layer thickness increases beyond this these differences be-
come less and preferential plating does not take place on the protrusions.

An attempt was made to take advantage of this by charging the electrode with
current pulses rather than with continuous current. The current pulse was only
long enough so that the diffusion layer thickness still followed the surface ir-
regularities. The off time was long enough to allow the diffusion layer to de-
cay. Such treatment did give smoother zinc deposits. This type of charging has
been tried by others. Romanov (66) noted that such charging improved the cycle
life of nickel-zinc cells. Wales (80) has studied its effects on silver-zinc
batteries.

Later, (61b) these same ideas were applied to the type of deposit obtained at a
vertical zinc electrode. Zincate solutions are more dense than KOH solutions
depleted of zincate. Consequently, the zincate depleted solutions tend to rise to
the top. On a vertical electrode the zinc plated out in a mossy form (activation
control) at the bottom of the electrode where the zincate concentration was great-
est and in a dendritic form (diffusion control) at the top of the electrode where
the solution was depleted in zincate.

The effect of the substrate also received attention (60c). The adherency (not the
type) of the deposit did depend on the substrate. However, the overpotential
also had an effect. Thus, with diffusion control (30 ma/cm^2) best adherency
was obtained on tin, while with activation control (15 ma/cm^2) best adherency
was obtained on lead. Amalgamation of the zinc also affected the adherency of
the deposit. These effects seemed to apply also after the surface had been covered
with a layer of zinc.

Another somewhat different interpretation of the relationship between the morphol-
ogy of the electrochemically deposited zinc and the overpotential or current
density has been suggested by Stachurski and Dalin (12). Here the presence of
small whiskers on the electrode surface are assumed to be present although no ex-
planation is given as to why these should be present. This may be related to the
structure of the substrate material, i.e., zinc metal. The different types of
zinc deposits are then explained in terms of the growth of these whiskers. At low

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overpotentials the process is activation controlled although there was also evidence for diffusion control at these same overpotentials at a rotating electrode. At higher overpotentials (more negative than $E_{1/2}$) the zinc deposit changes from mossy to dendritic. In a very narrow potential range in this region the diameter of the whiskers increases markedly. These thicker whiskers are the dendritic form of zinc deposit.

As current passes through the electrodes the diffusion layer thickness increases with time. At the same time the whiskers grow in length. If the growth of the whisker is equal to the rate of increase of diffusion layer thickness, the whisker then follows the expanding diffusion layer and growth continues and this produces the mossy zinc deposit. If, however, for some reason or other the whisker growth lags behind the expansion of the diffusion layer, then the whisker will be concentration polarized. That is, it may become starved of zincate and growth will stop.

In the case where the growth of the whisker is equal to the growth of diffusion layer, the tip of the whisker can remain under activation control. There are other parts of the whisker, however, which are subject to diffusion control. That is, there can be a concentration gradient in the solution from the tip of a whisker to the substrate metal or electrode material. This means that parts of the whisker nearer to the substrate metal may be subject to diffusion control while the tip of the whisker is under activation control. If the overpotential is increased the diffusion layer boundary expands away from the tip of the whisker and then the whole whisker is under diffusion control. This gives rise to dendrites.

This work, and these models, serve as a useful beginning to a better understanding of the charging process at the zinc electrode in alkaline solution.

In addition to these models, other information on the overvoltage of these cathodic processes is available (18). This was obtained by two different experimental approaches. The concentration range studied was 30-45% KOH all containing 0.5 M ZnO. It was found that the limiting current density before hydrogen was freely evolved increased as the temperature increases from 10 to 30°C. This limiting current density was about 6 ma/cm^2 in 30% KOH at room temperature and is less than half the limiting current density for the anodic reaction. It decreases somewhat as the KOH concentration increases to 40 and 45%. Furthermore, the overvoltage for the hydrogen evolution was 50-55 mv. Thus the reduction of zincate at the zinc electrode must be carried out at a low current density if the evolution of hydrogen is to be avoided, i.e., zinc electrodes must be charged at a low current density.

The situation is improved somewhat by amalgamating the zinc electrode. Amalgamated zinc electrodes can tolerate a higher limiting current density and the overvoltage at which zincate reduction takes place also is decreased. However, the effect of amalgamation tends to decrease with decreasing temperature. At 0°C there is little difference in the behavior of amalgamated and non-amalgamated zinc electrodes.

The above behavior is consistent with the idea that mass transport (of zincate ion) is the controlling factor in this cathodic process. The diffusion coefficient of the zincate ion decreases with decreasing temperature and increasing viscosity of the solution. The effect of amalgamation, however, indicates that the electrode material is also involved. This may be due to the increased hydrogen overvoltage when the electrode is amalgamated. This allows a higher zincate reduction overvoltage to prevail before hydrogen evolution begins. At $0^{o}C$ the solution viscosity is greater and diffusion of ions becomes more difficult. This leads to a lower limiting current density for a given reaction and amalgamation makes little difference.

This does not, however, account for the fact that with amalgamated electrodes the overvoltage is lower for the zincate reduction. This must be related to the nature of the zinc surface. It undoubtedly has a lower energy state than a plain zinc surface. The activity of the zinc atoms is less than one as a result of the amalgamation.

In working alkaline batteries containing zinc electrodes the charging process of the zinc electrode has been, and is a major problem. The bulk of the metallic zinc produced on charge likely comes from the reduction of zincate in the electrolyte although some amounts may come from the direct reduction of a film of zinc oxide or hydroxide. In some instances the zinc tends to become displaced and creep throughout the cell. This has often happened in cells cycling at a low current rate. Here the reduction is primarily activation controlled and a mossy type deposit is produced. At higher current rates the failure mode often is the formation of dendrites. Here the charging process is under diffusion control giving rise to dendritic deposit.

With this beginning of the understanding of the charging process other types of work suggest themselves. That is, the type of zinc deposit depends on conditions of current rate or overpotential. The plating industry has long relied on addition agents. With the above suggested models in mind such additives can be studied from a theoretical point of view, i.e., how they affect the overpotentials or the type of control that exists during cathodic treatment. Some work along this line has been done (12b). AC polarography was used to determine whether additives are adsorbed at the electrode surface and at what potentials. This has been done only at the dropping mercury electrode. It should be extended to a zinc metal electrode. Here some other technique would have to be used unless it were determined that the process is the same at a zinc electrode as at a mercury surface.

Another factor that needs study in connection with this process is the matter of electrolyte concentration. Most of the work cited above was done in 40-45% KOH solutions. This must be extended to more dilute KOH solutions to better understand the process in a working battery. In such a battery there may be considerable

variation in electrolyte concentration throughout the cell, especially at higher current rates. It is essential to know how the cathodic process is affected, if it is, at lower KOH concentrations. Other factors are temperature and amalgamation of the zinc electrode. Hardly any work has been reported in these areas.

There are complicating factors in a battery that will make the application of models for cathodic behavior only qualitative in degree. In such a battery there may be convective effects which need not be completely random. They may be local. They could, e.g., be induced by localized heating or depletion of OH^- ions. Furthermore, the presence of separators will have a modifying effect on the diffusion processes. Some work in this area has already been reported (12b, 12c). The separator does not change the relationship of type of control to the morphology of the deposit but it does change concentration gradients and diffusion processes.

D-- Miscellaneous

1. It has been observed that during the cycling of silver zinc cells the cycle life decreases with increasing depth of discharge, i.e., with increasing current density, (Fig. 13). This may be due to the different type of zinc morphology produced at different current rates (mossy, dendritic) as noted earlier in this report. This may also be due to a change in surface area or in particle size. It has been shown that the zinc electrode area increases with increasing current density on charge (cathodic) but decreases with increasing current density on discharge (anodic) (59). This was determined by measuring the double layer capacitance of a zinc electrode during cycling. No explanation is given for this change in surface area. This may, of course, merely be another way of looking at the differences in zinc crystal morphology.

The data on Fig. 13 should be compared only internally and not with that obtained from other silver-zinc cells. The explanation for the poor performance at temperatures below 30°F is that the zinc electrode does not accept charge well at these temperatures. This is consistent with zinc electrode data referred to earlier in this report (18) which show that at lower temperatures hydrogen begins to be evolved at a low current density and amalgamation of the zinc does little to change this. The problem here is one of being content with a very low charging current rate or of finding some way of raising the hydrogen overvoltage on zinc at low temperatures.

At higher temperatures the cells are limited by the loss of negative material (zinc) or by shorting. This is related to the current density and the type of zinc deposit as noted earlier.

2. In the operation of a sealed zinc-alkaline battery it would be advantageous to have the capacity of the cell limited by the positive active material so that on over-charge oxygen would be evolved at the positive electrode and then combine with the zinc electrode. This is the principle used in some sealed nickel-cadmium cells.

Some work on this problem has been done at the Yardney Company (75) and at the Delco-Remy plant (47). It was found that the rate of recombination of oxygen with zinc in a silver-zinc cell is greater during over-charge than during stand. Evidence was obtained for the assumption that the rate of recombination is due to two factors: (a) surface oxidation; and (b) diffusion of oxygen through the electrolyte. Aside from this, little has been published on this particular reaction. If this reaction is to be used in working cells, a good deal more work will have to be done to determine rates of reaction and the factors that influence them.

SOLUBILITY OF ZINC OXIDES

The solubility of several types of zinc oxide in KOH solutions was measured at -3°C. The techniques used and the characterization of these oxides were described in the Third Quarterly Technical Progress Report. The results are given below.

Solubility of ZnO in KOH Solutions at -3°C.

KOH → Type ZnO		19.72	29.50	36.77	39.25	44.47
XX	503	2.09	4.13	5.81	6.50	8.03
XX	602	2.08	4.14	5.87	6.57	8.09
USP	12	2.17	4.21	5.89	6.57	8.15
KADOX	15	2.22	4.29	6.00	6.69	8.27

There is little difference in solubility among the various types of ZnO. The results at -3°C are very close to the values at 15°C and 25°C reported earlier.

PROGRAM FOR NEXT QUARTER

Since the solubilities of the various types of zinc oxide are so similar only a few selected types will be used to measure solubility at $50^{o}C$. This work will be completed during the next quarter.

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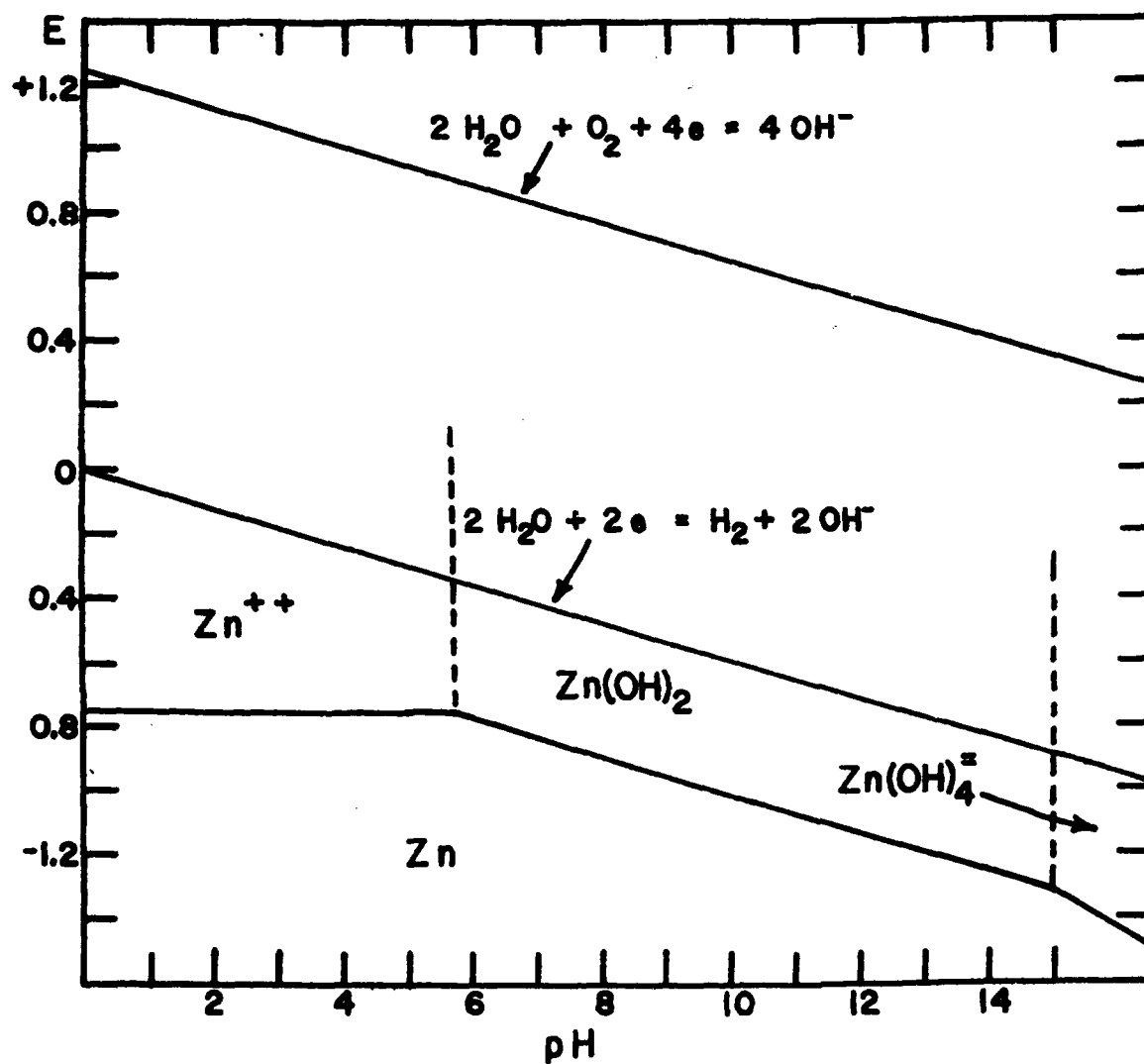
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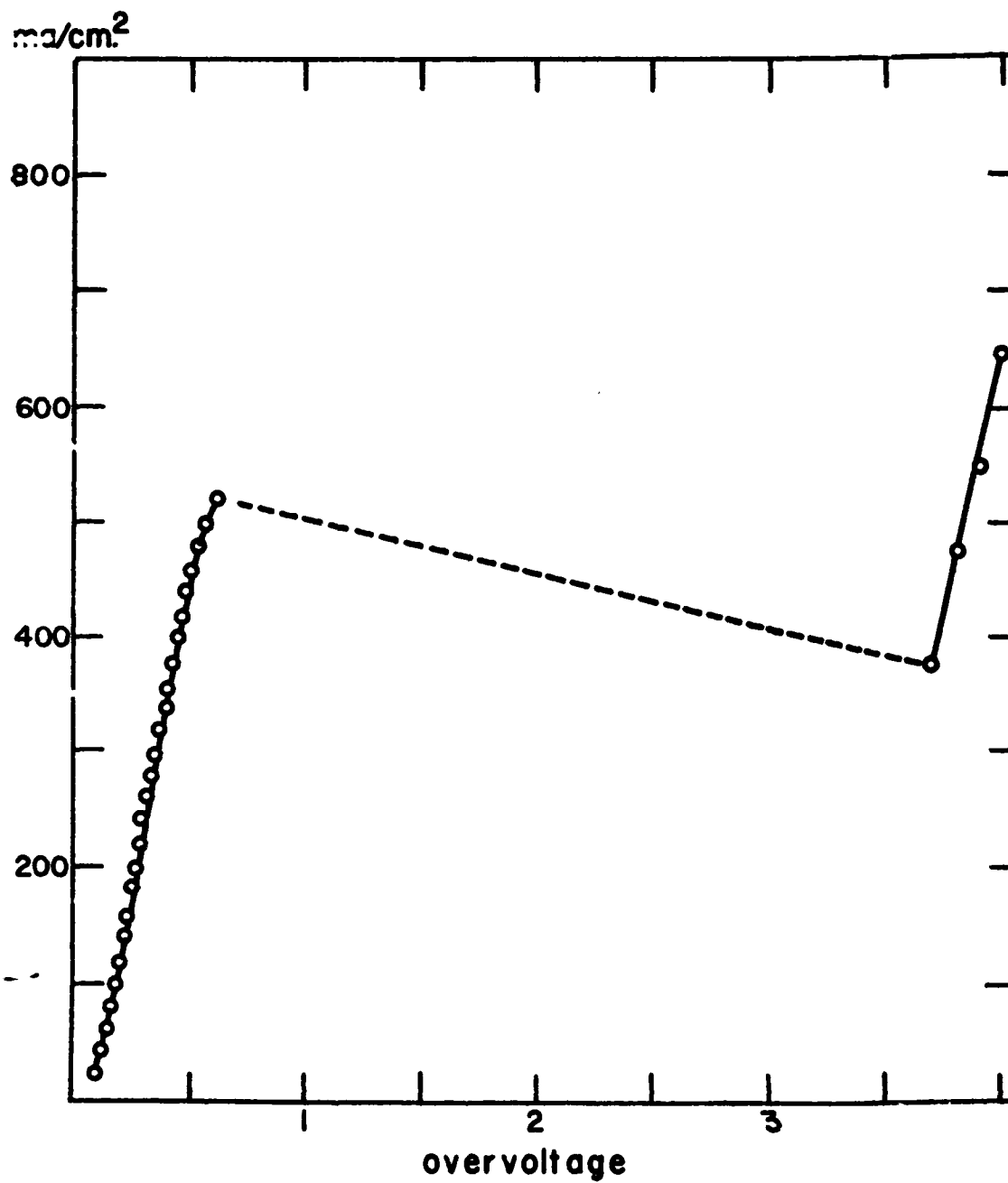Figure 1. Potential – pH diagram for the zinc electrode at 25°C.

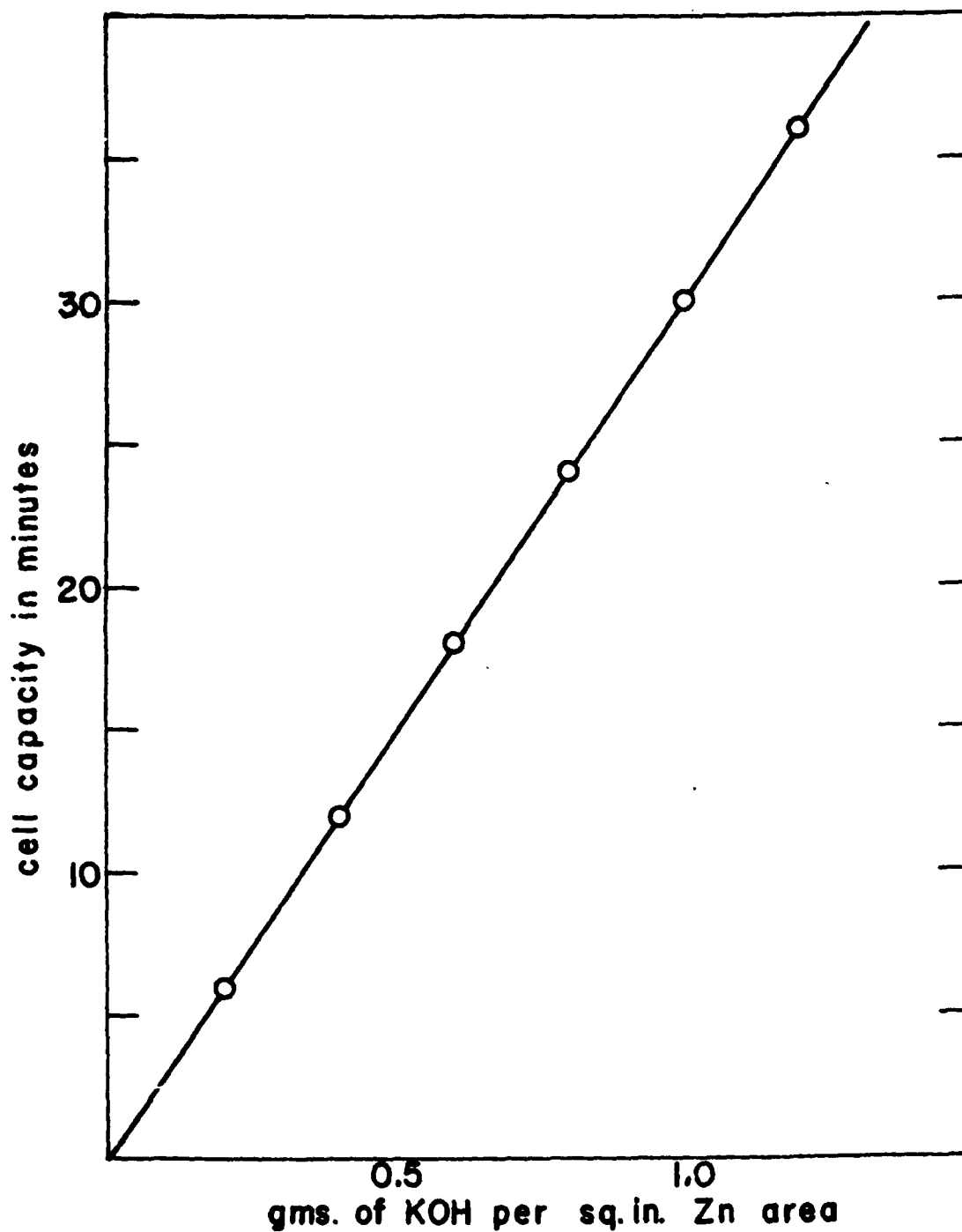Figure 2. Current – voltage curve for the anodic treatment of a zinc electrode in KOH at room temperature.

Figure 3. Capacity of a zinc electrode as a function of the amount of KOH per unit area of zinc electrode at 20°C. Current density is 470 ma/in². From reference (70).
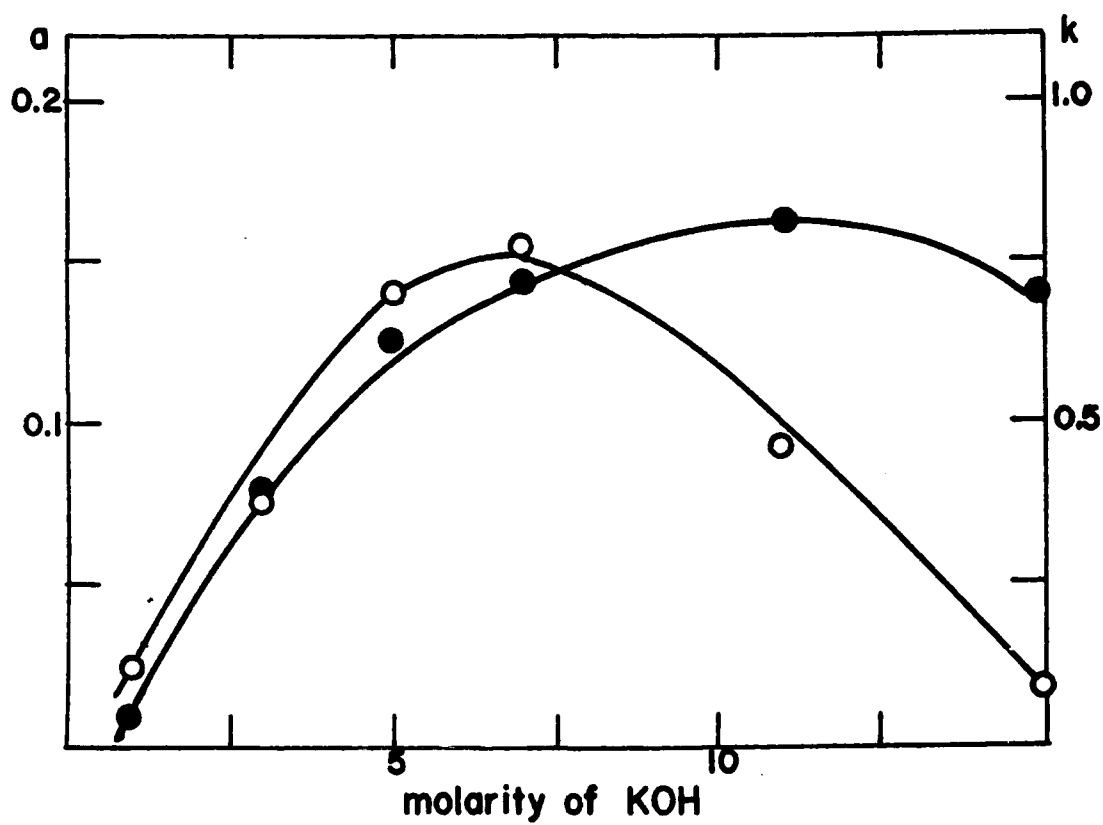
Figure 4. Variation of a and k with KOH concentration at 25°C. Open circles, a; closed circles, k. From reference (32).
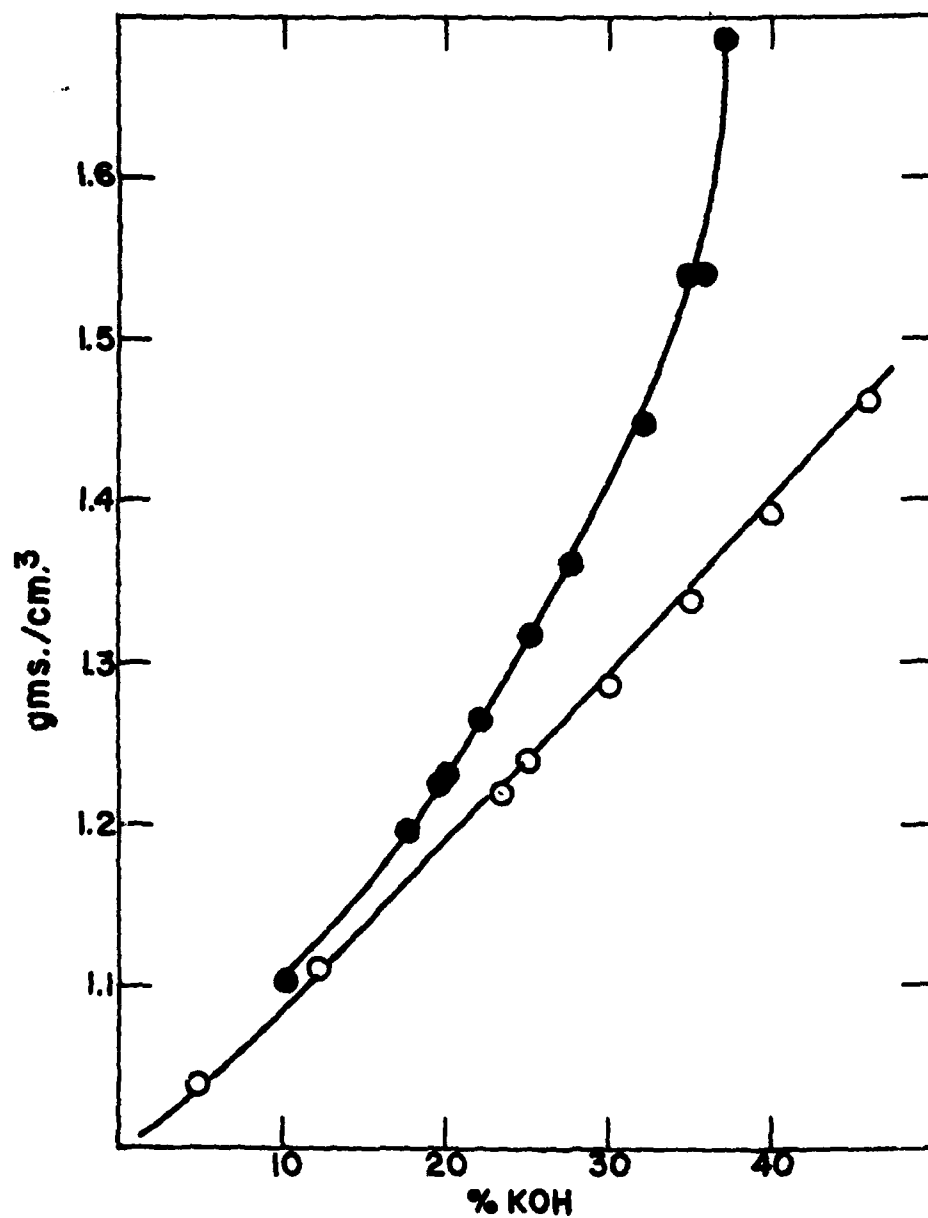
Figure 5. Density of KOH solutions at 25°C. Open circles, KOH solutions; closed circles, KOH solutions saturated with ZnO.
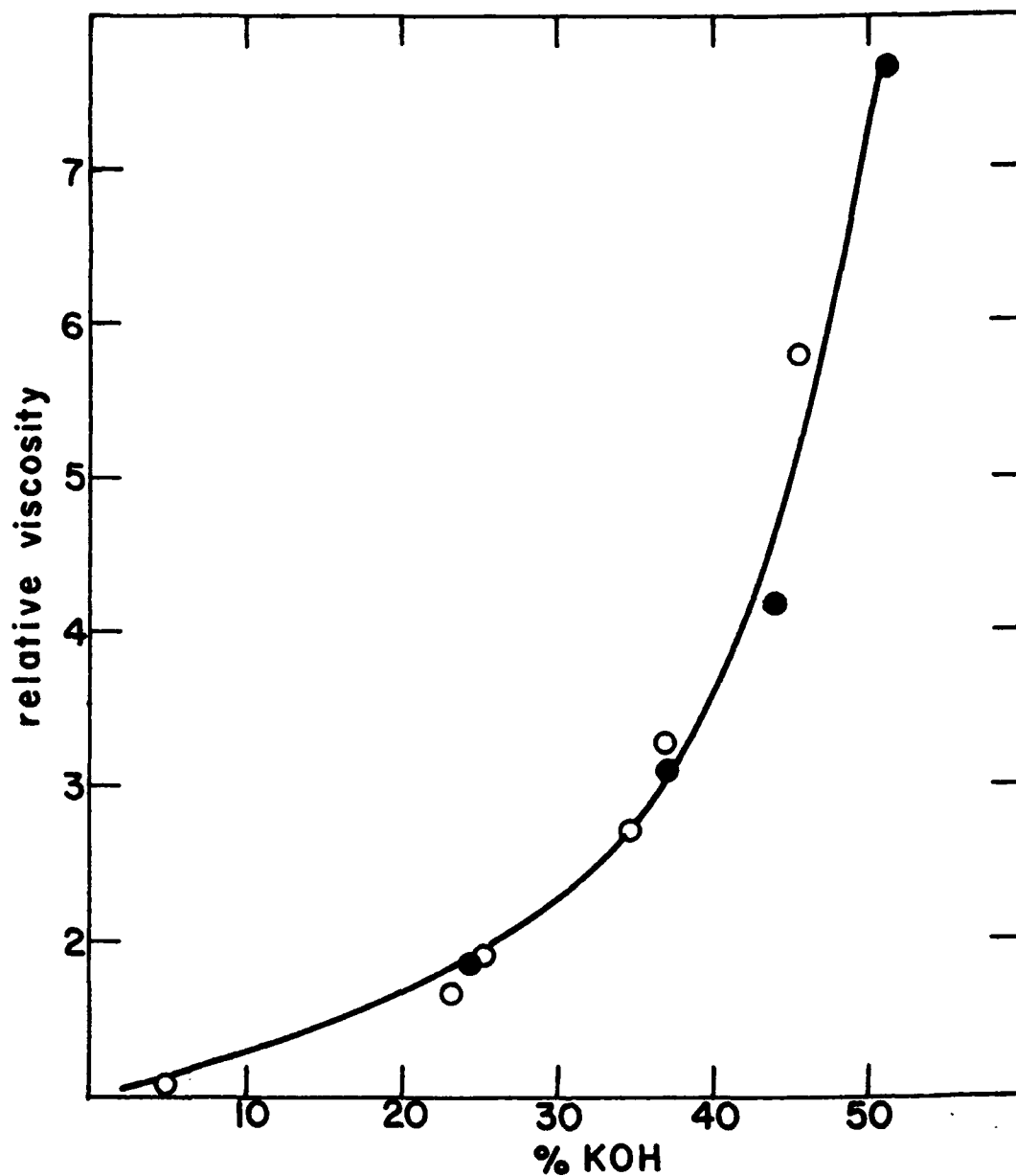
Figure 6. Relative viscosity of KOH solutions at 25°C. Open circles, KOH solutions; closed circles, KOH solutions saturated with ZnO.
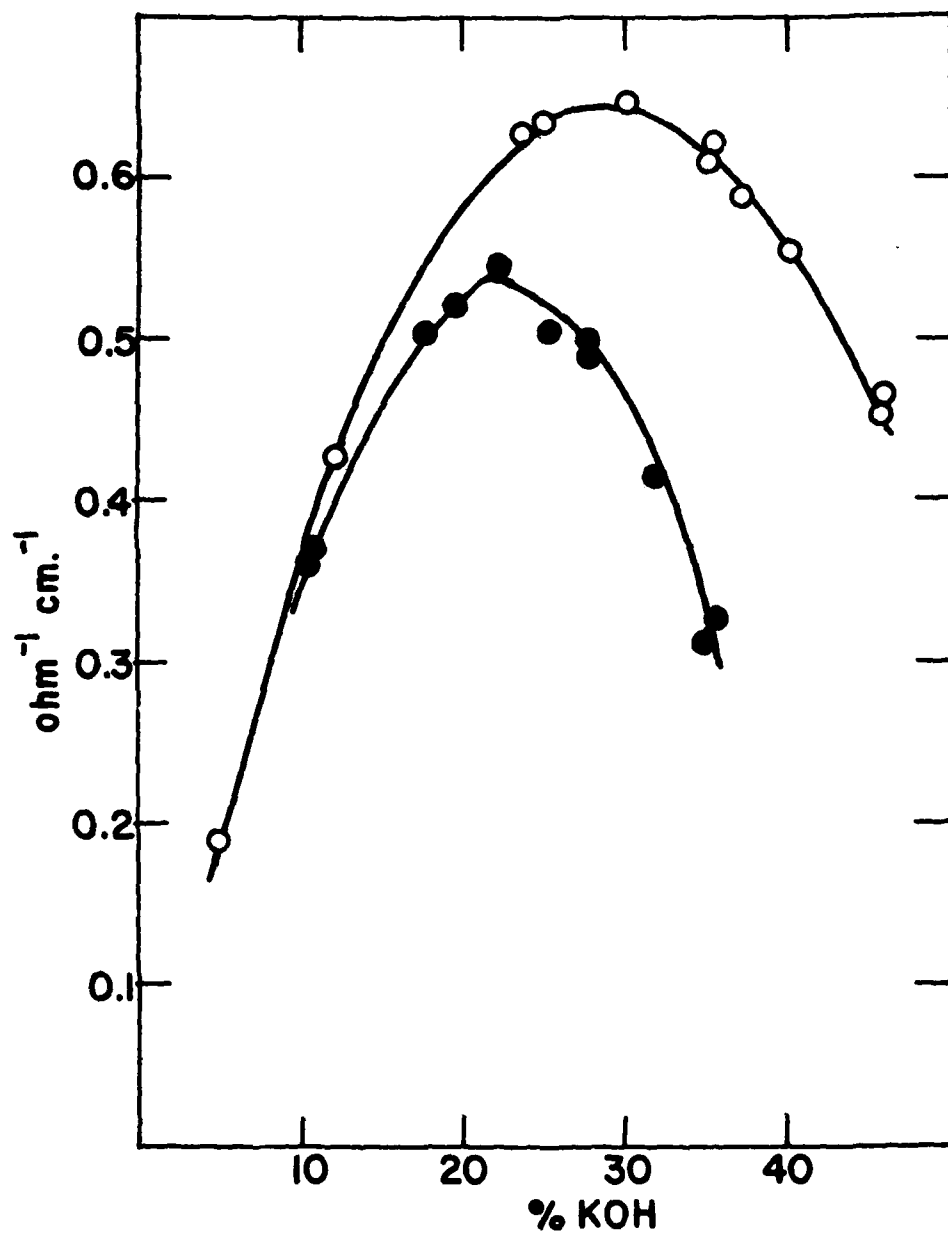
Figure 7. Specific conductance of KOH solutions at 25°C. Open circles, KOH solutions; closed circles, KOH solutions saturated with ZnO.

Figure 8. Surface tension of KOH solutions at 25°C. From reference (20).

Figure 9. Activities of KOH and NaOH solutions at 25°C. Solid lines, KOH; dotted lines, NaOH. From reference (1).

Figure 10. Limiting current density for zinc electrodes in KOH solutions. Circles, zinc; squares, amalgamated zinc; open symbols, no zincate; closed symbols, saturated with zincate.

Figure 11. Anodic overvoltage for zincate formation at a zinc electrode. Symbols are the same as for Figure 10.

Figure 12. Capacity of zinc electrodes per unit weight of KOH as a function of temperature. From reference (70).

Figure 13. Solubility of reagent grade ZnO in KOH solutions.

Figure 14. Cycle life of silver-zinc batteries at room temperature. From reference (42).

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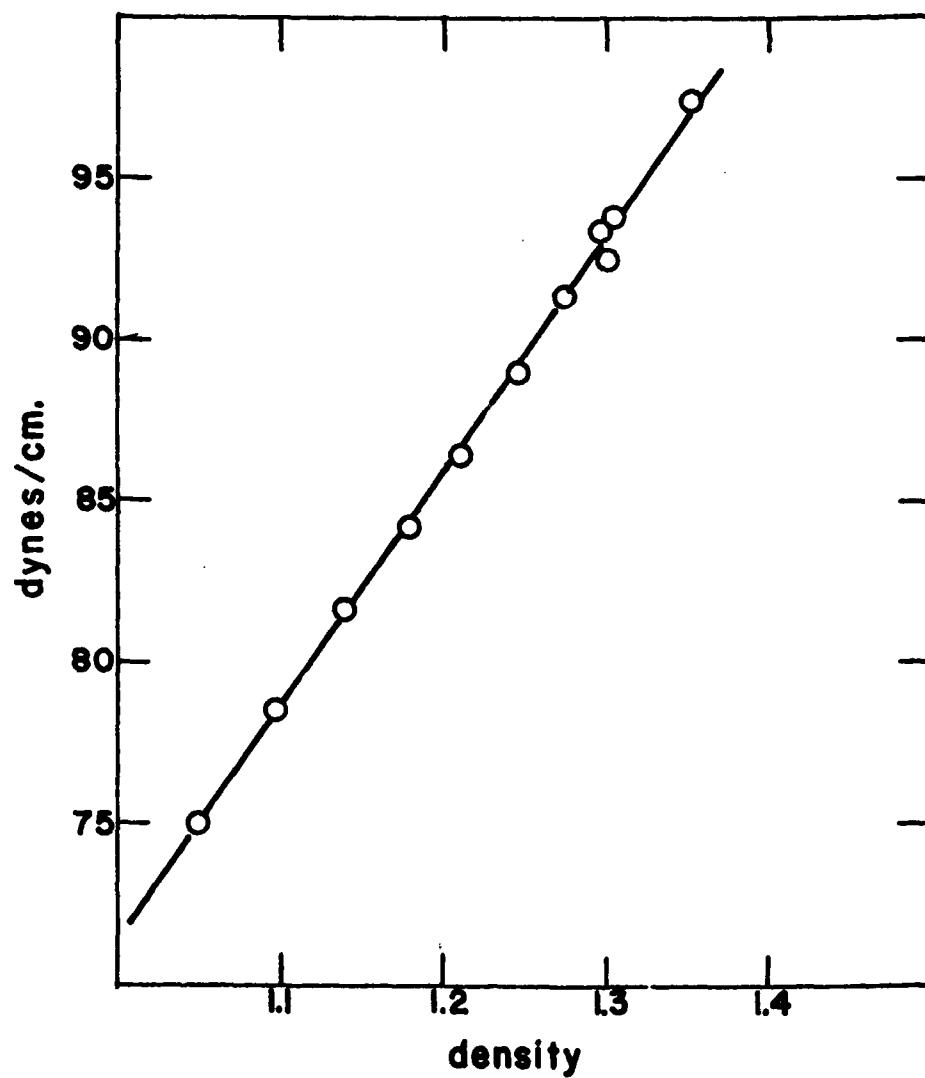
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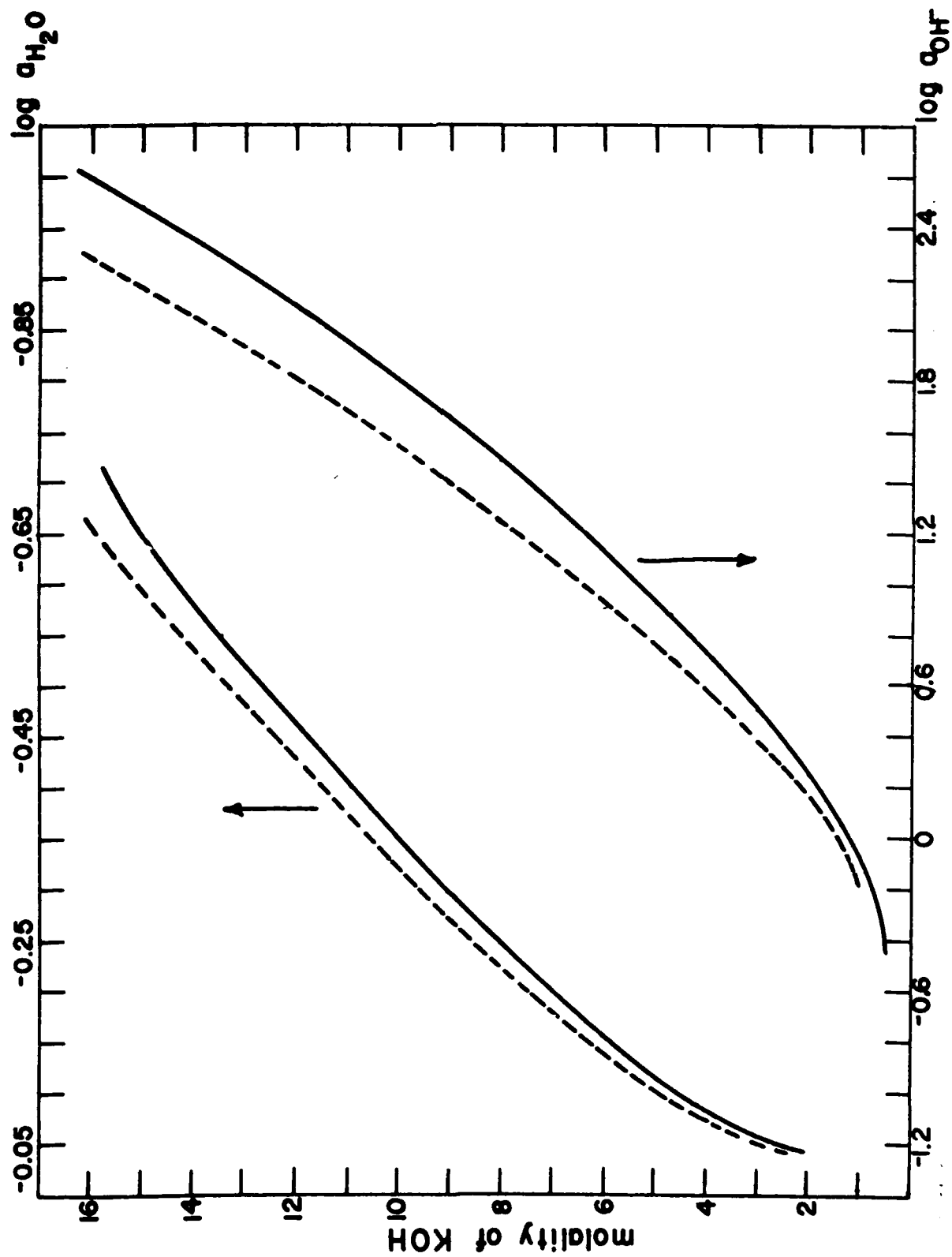
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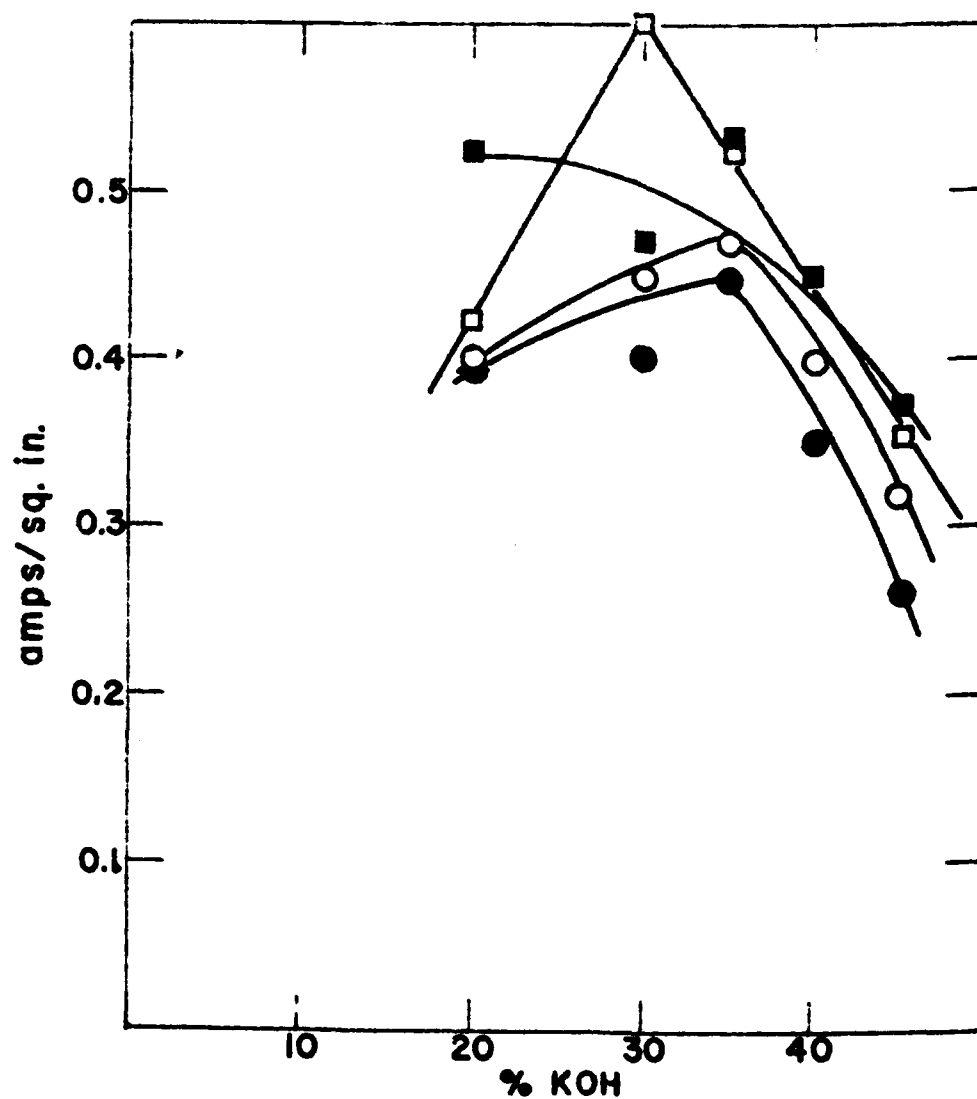
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Figure 10. Limiting current density for zinc electrodes in KOH solutions.
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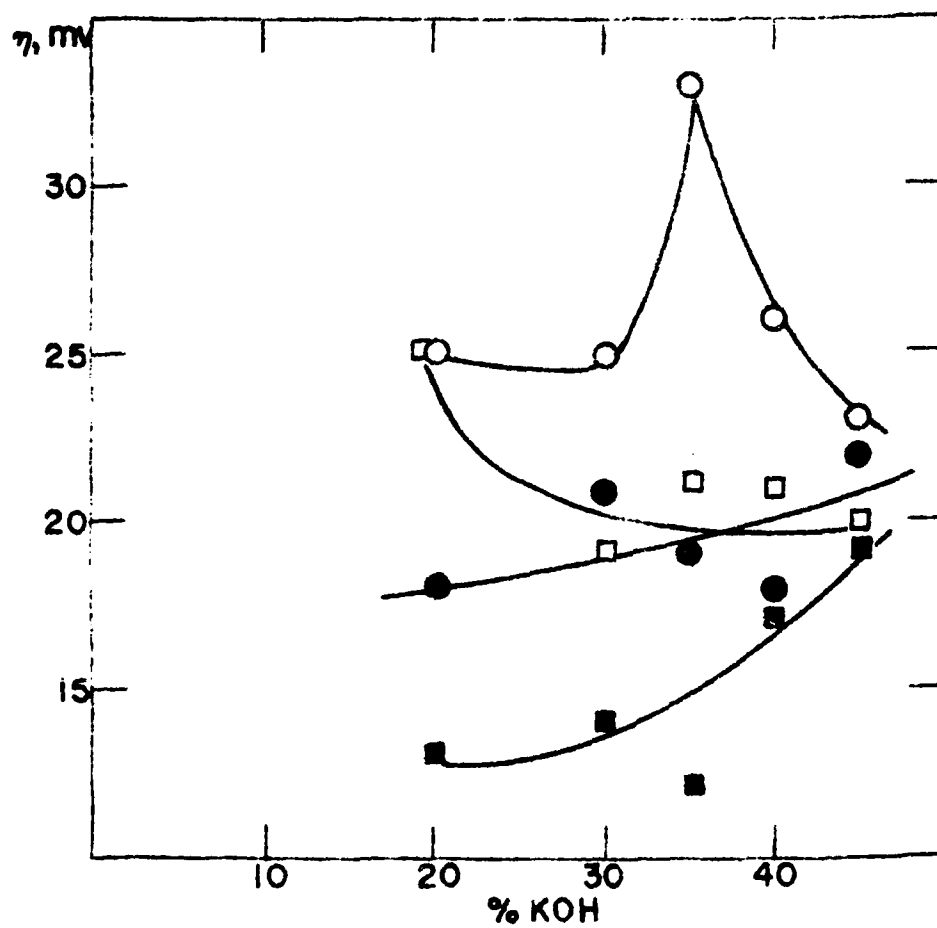no zincate; closed symbols, saturated with zincate.

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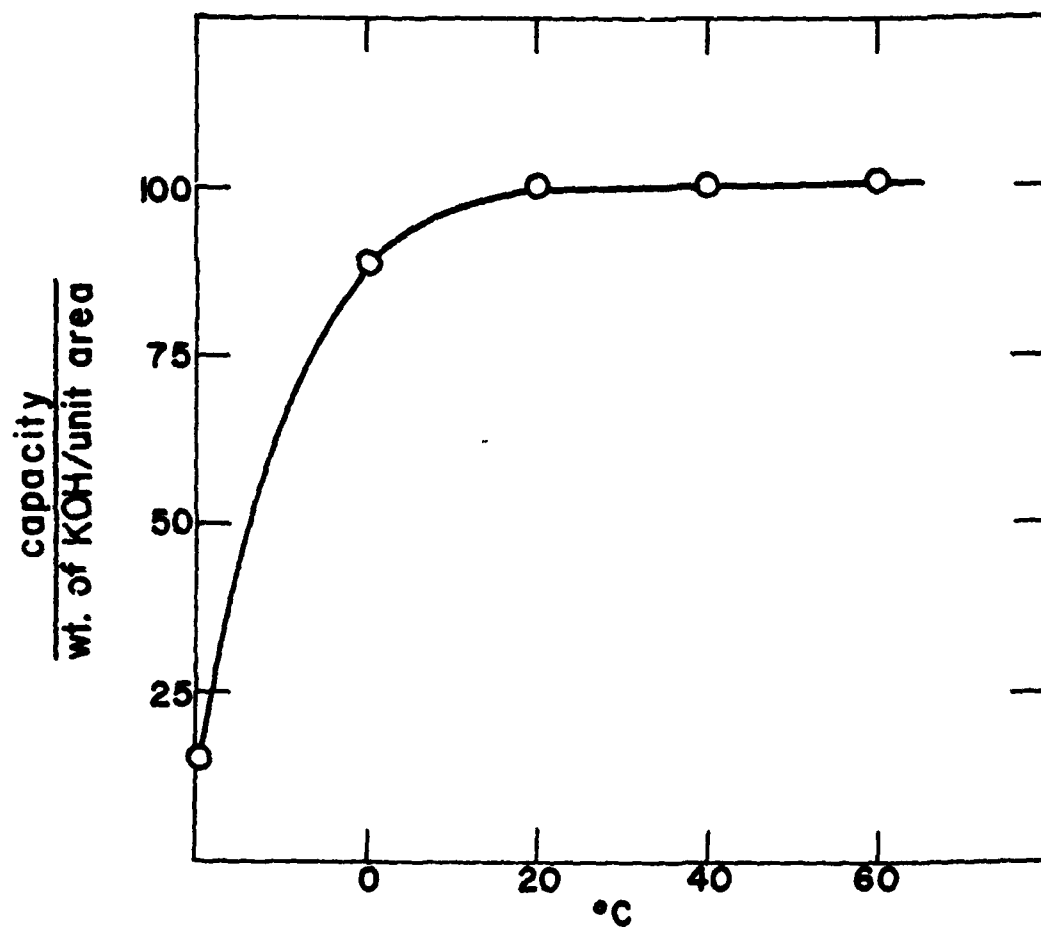
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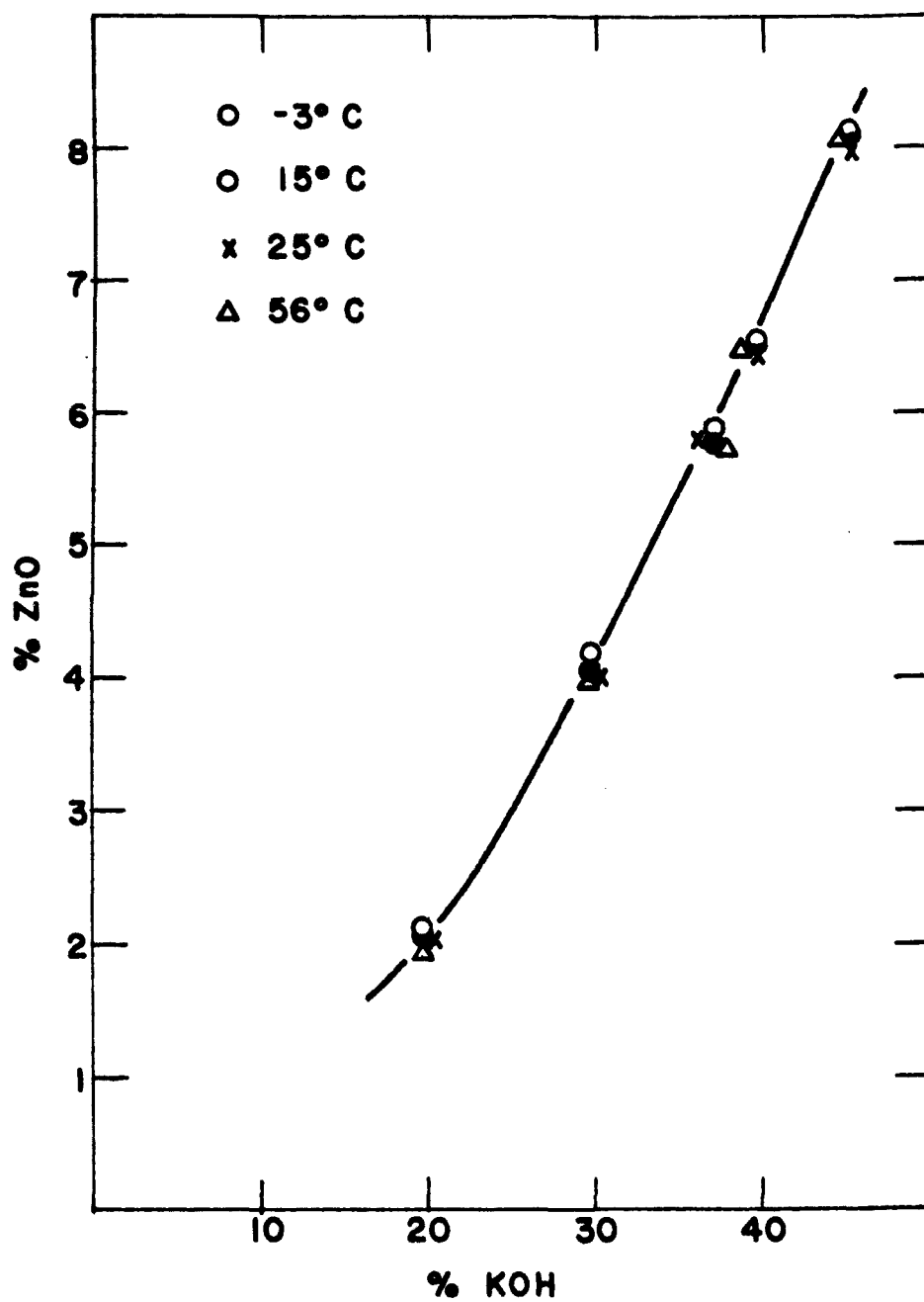
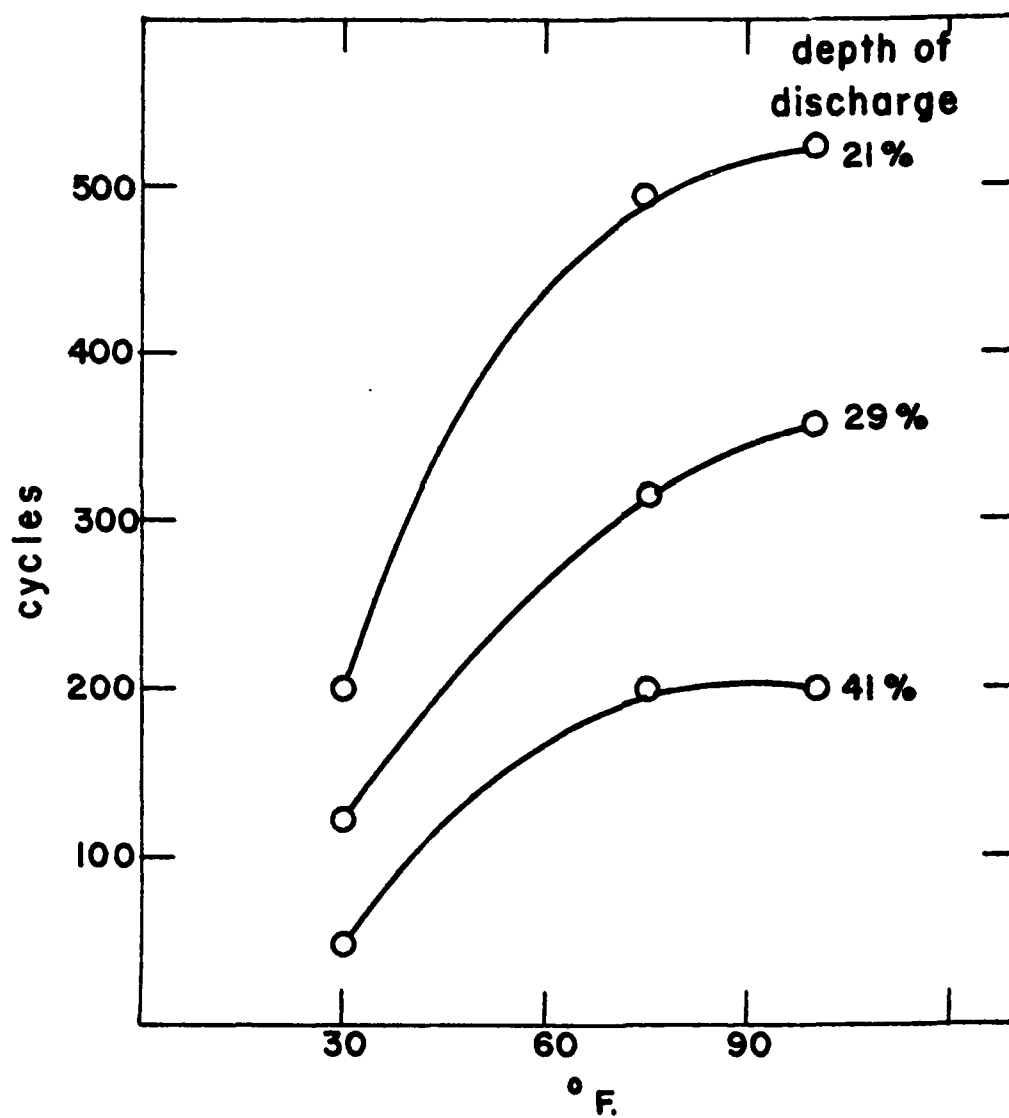**Figure 12.** Solubility of reagent grade ZnO in KOH solutions.

Figure 14. Cycle life of silver zinc batteries at room temperature. From reference (42).

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13. ABSTRACT

A review of the literature dealing with zinc electrode processes is given. The processes reviewed are: anodic behavior; cathodic behavior; and corrosion behavior. Suggestions are also made as to areas where experimental information is, as yet, not incorporated in the published literature.

The solubility values of various types of zinc oxide in KOH solutions at about 0° C. is presented.

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14 KEY WORDS	LINK A		LINK B		LINK C	
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